



VERIFICATION

The undersigned, of the below address, hereby certifies that he/she well knows both the English and Japanese languages, and that the attached is an accurate English translation of the Japanese Patent application filed on March 24, 2004 under No. P2004-086630.

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 4th day of July, 2008.

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## [Document Name] Claims

[Claim 1] A prepreg obtained by impregnating a resin composition into a fiber base material with a thickness of 5-100  $\mu\text{m}$ , wherein said resin composition is a resin composition comprising (a) a polyamideimide resin, (b) a thermosetting resin and (c) a hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant.

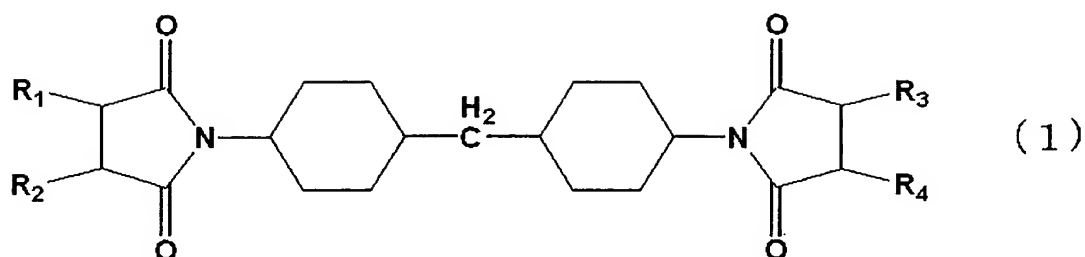
[Claim 2] A prepreg according to claim 1, wherein said fiber base material is a glass cloth.

[Claim 3] A prepreg according to claim 1 or 2, wherein said (c) hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant is one or more types of antioxidant selected from the group consisting of butylated hydroxyanisole, 2,6-di-t-butyl-4-ethylphenol, 2,2'-methylene-bis(4-methyl-6-t-butylphenol), 4,4'-thiobis-(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate)methane, dilauryl thiodipropionate and distearyl thiodipropionate.

[Claim 4] A prepreg according to any one of claims 1 to 3, wherein (a) polyamideimide resin is a siloxane-modified polyamideimide resins.

[Claim 5] A prepreg according to any one of claims 1 to 4, wherein said (a) polyamideimide resin is a polyamideimide resin including the structure represented by the following general formula (1).

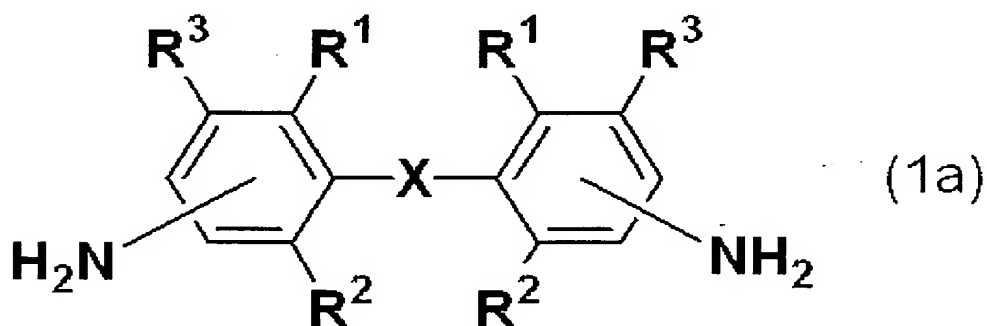
[Chemical Formula 1]



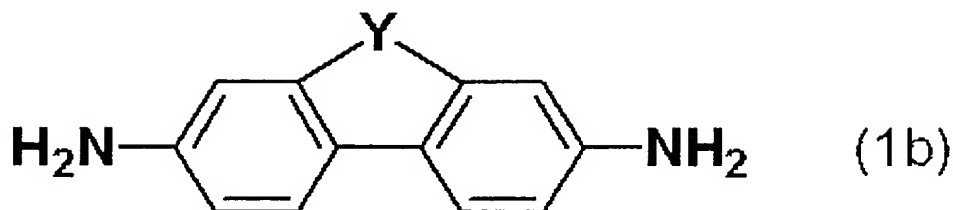
[wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each represent a carbon atom from a portion of the cyclic or linear structure composing the polyamideimide resin.]

[Claim 6] A prepreg according to any one of claims 1 to 4, wherein said (a) polyamideimide resin is a polyamideimide resin obtained by reacting a diisocyanate compound with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine with two or more aromatic rings represented by the following general formula (1a) or (1b) and a siloxane diamine, with trimellitic anhydride, and wherein said (b) thermosetting resin is an epoxy resin with two or more glycidyl groups.

[Chemical Formula 2]

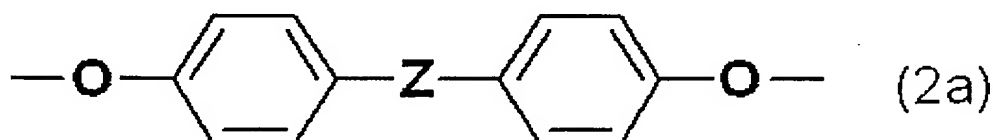


[Chemical Formula 3]

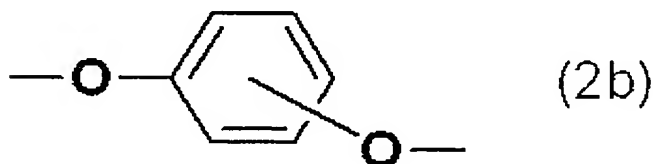


(wherein X represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, a single bond, a divalent group represented by the following general formula (2a) or a divalent group represented by the following general formula (2b), Y represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each independently or identically represent hydrogen, hydroxyl, methoxy, methyl or halogenated methyl.

[Chemical Formula 4]



[Chemical Formula 5]



wherein Z represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group, carbonyl group, or a single bond.)

[Claim 7] A metal foil-clad laminate obtained by stacking a prescribed number of prepregs according to any one of claims 1 to 6, situating a

metal foil on either or both sides thereof and subjecting the stack to heat and pressure.

[Claim 8] A printed circuit board obtained by forming a circuit on said metal foil-clad laminate according to claim 7.

[Document Name] Specification

[Title of the Invention] PREPREG, METAL CLAD LAMINATE,  
AND PRINTED CIRCUIT BOARD USING SAME

[Field of the Invention]

5           [0001]

The present invention relates to a prepreg and to a metal foil-clad laminate and printed circuit board that employ it.

[Prior Art]

10           [0002]       Laminates for printed circuit boards are formed by stacking a prescribed number of prepregs comprising an electrical insulating resin composition as the matrix, and subjecting them to heat and pressure for integration.

15       Metal-clad laminates are used for formation of printed circuits by a subtractive process. Metal-clad laminates are fabricated by stacking a metal foil such as copper foil on a surface (either or both surfaces) of a prepreg and subjecting the stack to heat and pressure. As electrical insulating resins there are commonly used thermosetting resins such as phenol resins, epoxy resins, polyimide resins, bismaleimide-triazine resins and the like. Thermoplastic resins such as fluorine resins or  
20       polyphenylene ether resins are also sometimes used.

          [0003]       On the other hand, with the increasing popularity of data terminal devices such as personal computers and cellular phones there is a trend toward miniaturization and high-densification of the printed circuit boards mounted therein. The mounting methods are  
25       advancing from pin-insertion types to surface-mounted types, and also to area array types of which BGA (ball grid arrays) using plastic boards

are a typical example. In boards where bare chips such as BGA are directly mounted, connection between the chips and boards is commonly achieved by wire bonding using thermosonic bonding. In such cases, the board on which the bare chip is mounted is exposed to high temperatures of 150°C and above, and therefore the electrical insulating resin must have some degree of heat resistance.

[0004] As lead-free solders become more common for environmental reasons, the melting points of solders are increasing as a result. Thus, even higher heat resistance is demanded for boards. Demand for halogen-free materials is also increasing, thus precluding the use of bromine-based flame retardants. Moreover, the "repair properties" allowing mounted chips to be removed are often required. During repair, the boards are subjected to about the same level of heating as during chip mounting, after which further heat treatment is carried out for remounting of chips. Such treatment has often resulted in peeling between the fiber material and resin in conventional insulating resin systems. Thus, boards exhibiting repair properties must also have cycling heat shock-resistant properties at high temperatures.

[0005] Prepregs have been proposed that exhibit excellent heat shock resistance, reflow resistance and crack resistance, and improved microwiring formation properties, by impregnating a resin composition comprising a polyamideimide as an essential component into the fiber material (see Patent Literature 1). Moreover, in printed circuit board, with densification of the circuit, the migration of the metal is put easily, and the demand of so-called electrolytic corrosion

resistance becomes severe. In prepreg which uses epoxy resin, the improvement of an electrolytic corrosion resistance by addition of an antioxidant is proposed (see Patent Literature 2).

[0006] Also, with the trend toward greater miniaturization and higher performance of electronic devices, it is becoming necessary to house part-mounted printed circuit boards in increasingly limited spaces. This is accomplished by methods of arranging multiple printed circuit boards in stacks and connecting them alternately with wire harnesses or flexible wiring boards. There are also used rigid-flex boards which are layered combinations of polyimide-based flexible boards and conventional rigid boards.

[Patent Literature 1] Japanese Unexamined Patent Publication No. 2003-55486

[Patent Literature 2] Japanese Unexamined Patent Publication No. H3-43413

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0007] The present invention solves the problems of the prior art described above, and is to provide a printed circuit board which metal migration is hard to happen, with excellent electrolytic corrosion resistance, dimensional stability and heat resistance and the ability to be bent and housed at high density in electronic device packages, by impregnating a thin fiber base material with a resin having excellent adhesion with metal foils or fiber base materials, excellent heat resistance and high pliability, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.



## [Means for Solving the Problem]

[0008]

The present invention relates to the following.

(1) A prepreg obtained by impregnating a resin composition into a fiber base material with a thickness of 5-100  $\mu\text{m}$ , wherein said resin composition is a resin composition comprising (a) a polyamideimide resin, (b) a thermosetting resin and (c) a hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant.

(2) A prepreg according to (1), wherein said fiber base material is a glass cloth.

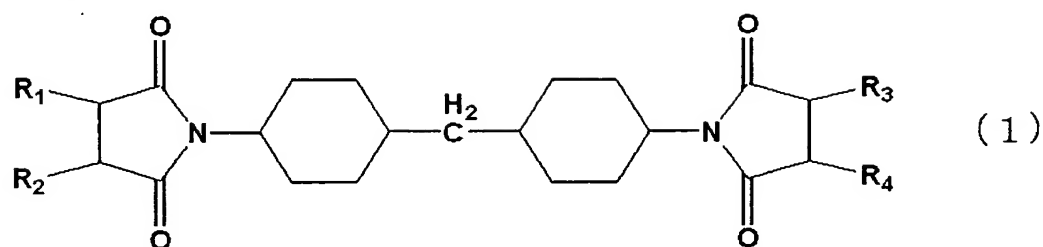
(3) A prepreg according to (1) or (2), wherein said (c) hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant is one or more types of antioxidant selected from the group consisting of butylated hydroxyanisole, 2,6-di-t-butyl-4-ethylphenol, 2,2'-methylene-bis(4-methyl-6-t-butylphenol), 4,4'-thiobis-(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate)methane, dilauryl thiodipropionate and distearyl thiodipropionate.

(4) A prepreg according to any one of (1) to (3), wherein said (a) polyamideimide resin is a siloxane-modified polyamideimide resins.

(5) A prepreg according to any one of (1) to (4), wherein said (a) polyamideimide resin is a polyamideimide resin including the structure represented by the following general formula (1).

[0009]

[Chemical Formula 1]

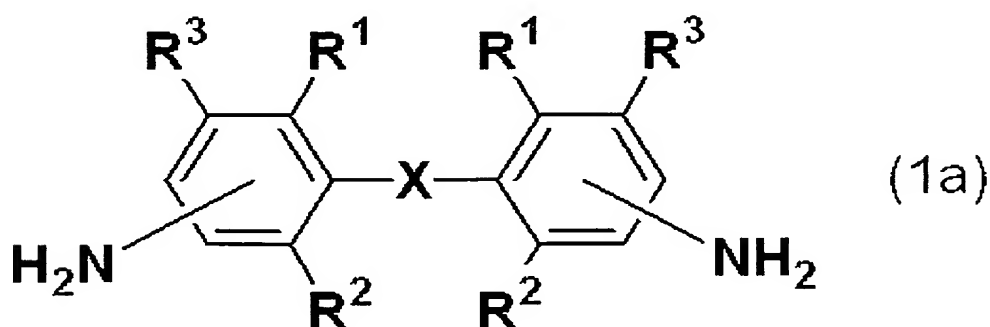


[wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each represent a carbon atom from a portion of the cyclic or linear structure composing the polyamideimide resin.]

(6) A prepreg according to any one of (1) to (4), wherein said (a) polyamideimide resin is a polyamideimide resin obtained by reacting a diisocyanate compound with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine with two or more aromatic rings represented by the following general formula (1a) or (1b) and a siloxane diamine, with trimellitic anhydride, and wherein said (b) thermosetting resin is an epoxy resin with two or more glycidyl groups.

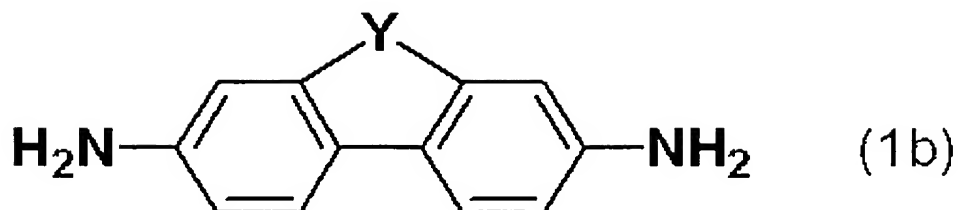
[0010]

[Chemical Formula 2]



[0011]

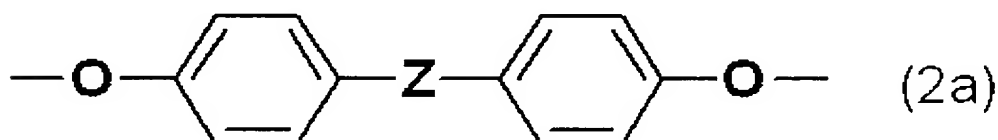
[Chemical Formula 3]



(wherein X represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, a single bond, a divalent group represented by the following general formula (2a) or a divalent group represented by the following general formula (2b), Y represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group or carbonyl group, and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each independently or identically represent hydrogen, hydroxyl, methoxy, methyl or halogenated methyl.

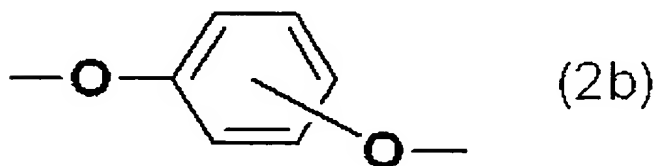
[0012]

[Chemical Formula 4]



[0013]

[Chemical Formula 5]



wherein Z represents a C1-3 aliphatic hydrocarbon group, C1-3 halogenated aliphatic hydrocarbon group, sulfonyl group, ether group, carbonyl group, or a single bond.)

(7) A metal foil-clad laminate obtained by stacking a prescribed number of prepregs according to any one of (1) to (6), situating a metal foil on either or both sides thereof and subjecting the stack to heat and pressure.

5 (8) A printed circuit board obtained by forming a circuit on said metal foil-clad laminate according to (7).

[Effects of the Invention]

[0014]

10 The metal foil-clad laminate and the printed circuit board obtained by using the prepreg of the present invention have the ability to be bent and have flame retardance in halogen free, excellent dimensional stability and heat resistance. These also have excellent electrolytic corrosion resistance because metal migration is hard to happen.

[Best Mode for Carrying Out the Invention]

15 [0015]

The prepreg of the present invention is the prepreg obtained by impregnating a resin composition into a fiber base material with a thickness of 5-100  $\mu\text{m}$ , wherein said resin composition is a resin composition comprising (a) a polyamideimide resin, (b) a thermosetting resin and (c) a hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant.

[0016]

20 It is preferred that the (a) polyimide resins in the present invention is a siloxane-modified polyamideimide resins. It is also preferred that the (a) polyimide resins in the present invention is a polyamideimide resins having the structure represented by the foregoing general formula (1).

[0017]

As (a) polyamideimide resin used in the present invention, the polyamideimide resin obtained by reacting an aromatic diisocyanate with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a diamine with two or more aromatic rings (aromatic diamine) and a siloxane diamine with trimellitic anhydride is preferred. As the polyamideimide resins having the structure represented by the foregoing general formula (1), the polyamideimide resin obtained by reacting an aromatic diisocyanate with a mixture containing a diimidedicarboxylic acid obtained by reacting a mixture containing a 4, 4'-diamino dicyclo hexyl methane, a diamine with two or more aromatic rings (aromatic diamine) and a siloxane diamine with trimellitic anhydride is preferred. Example for 4, 4'-diamino dicyclo hexyl methane includes WONDAMINE (trade name of New Japan Chemical Co., Ltd.).

[0018]

For synthesis of a siloxane-modified polyamideimide resin with a siloxane structure, the blending ratio of the diamine a with two or more aromatic rings and the siloxanediamine b is preferably  $a/b = 99.9/0.1-0/100$  (molar ratio), more preferably  $a/b = 95/5-30/70$  and even more preferably  $a/b = 90/10-40/60$ . If the blending proportion of the siloxanediamine b is too large, the Tg will tend to be reduced. If it is too small, on the other hand, a larger amount of varnish solvent will tend to remain in the resin from production of the prepreg.

[0019]

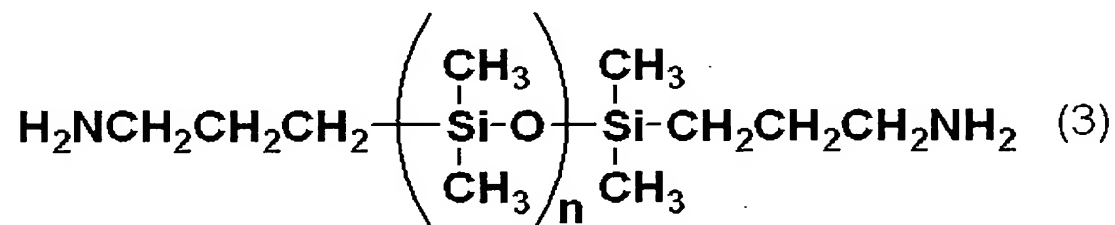
Examples of aromatic diamines include 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), bis[4-(3-aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, bis[4-(4-aminophenoxy)phenyl]methane, 4,4'-bis(4-aminophenoxy)biphenyl, bis[4-(4-aminophenoxy)phenyl]ether, bis[4-(4-aminophenoxy)phenyl]ketone, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 2,2'-dimethylbiphenyl-4,4'-diamine, 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine, 2,6,2',6'-tetramethyl-4,4'-diamine, 5,5'-dimethyl-2,2'-sulfonyl-biphenyl-4,4'-diamine, 3,3'-dihydroxybiphenyl-4,4'-diamine, (4,4'-diamino)diphenyl ether, (4,4'-diamino)diphenylsulfone, (4,4'-diamino)benzophenone, (3,3'-diamino)benzophenone, (4,4'-diamino)diphenylmethane, (4,4'-diamino)diphenyl ether and 3,3'-diaminodiphenyl ether.

[0020]

As siloxanediamines used in present invention there may be mentioned compounds represented by the following general formulas (3)-(6).

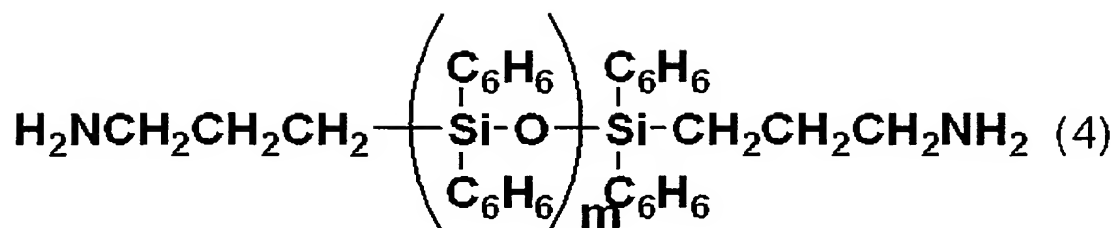
[0021]

[Chemical Formula 6]



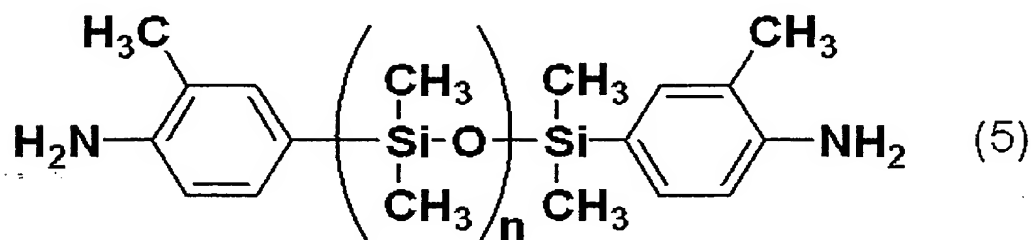
[0022]

[Chemical Formula 7]



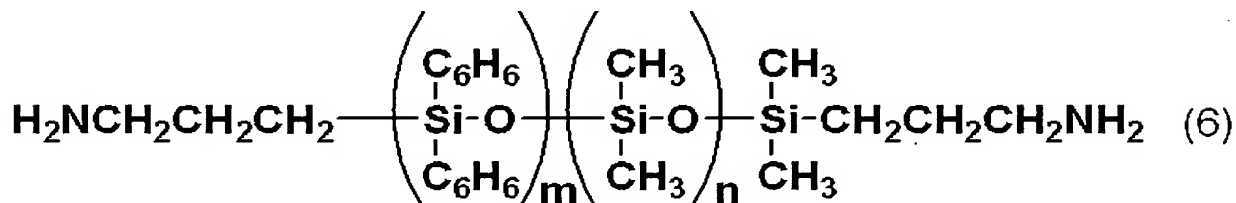
[0023]

[Chemical Formula 8]



[0024]

[Chemical Formula 9]



[0025]

Examples of siloxanediarnines represented by general formula (3) above include X-22-161AS (450 amine equivalents), X-22-161A (840 amine equivalents), X-22-161B (1500 amine equivalents) (all products of Shin-Etsu Chemical Co., Ltd.), BY16-853 (650 amine equivalents) and BY16-853B (2200 amine equivalents) (all products of Dow Corning Toray Silicone Co., Ltd.). Examples of siloxanediarnines represented by general formula (6) above include X-22-9409 (700

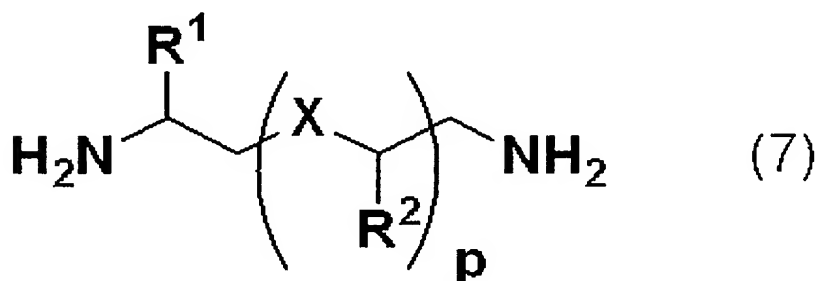
amine equivalents) and X-22-1660B-3 (2200 amine equivalents) (both products of Shin-Etsu Chemical Co., Ltd.).

[0026]

There may also be used an aliphatic diamine in addition to the  
5      aforementioned diamine. Examples of such aliphatic diamines include  
compounds represented by the following general formula (7).

[0027]

[Chemical Formula 10]



10      [In formula, X represents methylene, sulfonyl, ether, carbonyl or a  
single bond, R<sup>1</sup> and R<sup>2</sup> each represent hydrogen, alkyl, phenyl or  
substituted phenyl, and p represents an integer of 1-50.]

[0028]

As specific examples of R<sup>1</sup> and R<sup>2</sup> there are preferred hydrogen,  
15      C1-3 alkyl, phenyl and substituted phenyl, and examples of  
substituents bonded to phenyl include C1-3 alkyl, halogens and the like.  
From the standpoint of achieving both a low elastic modulus and high  
T<sub>g</sub>, the aliphatic diamine is preferably one wherein X in general  
formula (7) above is an ether group. Examples of such aliphatic  
20      diamines include JEFFAMINE D-400 (400 amine equivalents) and  
JEFFAMINE D-2000 (1000 amine equivalents, both products of San  
Techno Chemical Co., Ltd.).



[0029]

As diisocyanate compounds to be used for production of (a) polyamideimide resins of the present invention there may be mentioned compounds represented by the following general formula (8).

[0030]

[Chemical Formula 11]



[0031]

In the foregoing general formula (8), D is a divalent organic group with at least one aromatic ring, or a divalent aliphatic hydrocarbon group, and it is preferably at least one group selected from the group consisting of  $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$ , tolylene, naphthylene, hexamethylene, 2,2,4-trimethylhexamethylene and isophorone.

[0032]

As diisocyanate compounds represented by general formula (8) above there may be used aliphatic diisocyanate or aromatic diisocyanate compounds, but aromatic diisocyanate compounds are preferred, and combinations of both are especially preferred.

[0033]

Examples of aromatic diisocyanate compounds include 4,4'-diphenylmethanediisocyanate (MDI), 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, naphthalene-1,5-diisocyanate, 2,4-tolylene dimer and the like, with MDI being particularly preferred. Using MDI as an

aromatic diisocyanate can improve the flexibility of the obtained (a) polyamideimide resin.

[0034]

Examples of aliphatic diisocyanate compounds include hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate and isophorone diisocyanate.

[0035]

When an aromatic diisocyanate and aliphatic diisocyanate are used in combination, the aliphatic diisocyanate is preferably added at about 5-10 mol% with respect to the aromatic diisocyanate. Such use in combination can further improve the heat resistance of the obtained (a) polyamideimide resin.

[0036]

As (b) thermosetting resins to be used for the invention there may be mentioned epoxy resins, polyimide resins, unsaturated polyester resins, polyurethane resins, bismaleimide resins, triazine-bismaleimide resins and phenol resins. The (b) thermosetting resin is preferably used at 1-200 parts by weight with respect to 100 parts by weight of the (a) polyamideimide resin. In particular, the (b) thermosetting resin is preferably used at 1-200 parts by weight with respect to 100 parts by weight of the siloxane-modified polyamideimide resins. In the present invention, there are preferred a thermosetting resin having organic groups that can react with the amide groups of the the siloxane-modified polyamideimide resin, more preferred a glycidyl group-containing epoxy resins. The thermosetting resin is used at 1-200 parts by weight with respect to 100 parts by weight of the siloxane-modified

polyamideimide resin in the present invention, if the content of the thermosetting resin is less than 1 part by weight, the solvent resistance will tend to be inferior, if it exceeds 200 parts by weight, the Tg will be lower due to the unreacted thermosetting resin, leading to insufficient heat resistance and undesirable reduction in flexibility. Thus, the content of the thermosetting resin is more preferably 3-100 parts by weight and even more preferably 10-60 parts by weight to 100 parts by weight of the siloxane-modified polyamideimide resin.

[0037]

As epoxy resins there may be mentioned polyglycidyl ethers obtained by reacting epichlorhydrin with a polyhydric phenol such as bisphenol A, a novolac-type phenol resin or an orthocresol/novolac-type phenol resin or with a polyhydric alcohol such as 1,4-buthane diol, polyglycidyl esters obtained by reacting epichlorhydrin with a polybasic acid such as phthalic acid or hexahydrophthalic acid, N-glycidyl derivatives of compounds with amine, amide or heterocyclic nitrogenous bases, and alicyclic epoxy resins.

[0038]

By using an epoxy resin as the thermosetting resin in the present invention, it is possible to cure at a temperature of below 180°C, and to further improve the thermal, mechanical and electrical properties by reacting with amide groups of the polyamideimide resin. It is preferred to use as the epoxy resin a combination of an epoxy resin with two or more glycidyl groups and its curing agent, a combination of an epoxy resin with two or more glycidyl groups and its curing accelerator, or a combination of an epoxy resin with two or more

glycidyl groups and its curing agent and curing accelerator. A greater number of glycidyl groups is preferred, with 3 or more being more preferred. The content of the thermosetting resin will differ depending on the number of glycidyl groups, and the content may be lower with a larger number of glycidyl groups.

[0039]

The curing agent and curing accelerator for the epoxy resin are not particularly restricted so long as they react with the epoxy resin or promote its curing, and there may be used, for example, amines, imidazoles, polyfunctional phenols, acid anhydrides and the like. As amines there may be used dicyandiamide, diaminodiphenylmethane, guanylurea and the like. As polyfunctional phenols there may be used hydroquinone, resorcinol, bisphenol A and their halogenated forms, as well as novolac-type phenol resins and resol-type phenol resins that are condensates with formaldehyde. As acid anhydrides there may be used phthalic anhydride, benzophenonetetracarboxylic dianhydride, methylhymic acid and the like. As curing accelerators there may be used imidazoles such as alkyl-substituted imidazoles and benzimidazoles.

[0040]

The preferred amount of such a curing agent or curing accelerator is, in the case of an amine, an amount such that the equivalents of active hydrogen of the amine and epoxy equivalents of the epoxy resin are approximately equal. For an imidazole as the curing accelerator there is no simple equivalent ratio with active hydrogen, and the required amount is 0.001-10 parts by weight to 100 parts by weight of the

epoxy resin. In the case of a polyfunctional phenol or acid anhydride, the required amount is 0.6-1.2 equivalents of phenolic hydroxyl or carboxyl groups with respect to one equivalent of the epoxy resin. A small amount of such a curing agent or curing accelerator will leave some amount of uncured epoxy resin and will lower the T<sub>g</sub> (glass transition temperature), while a large amount will leave some amount of unreacted curing agent and curing accelerator, thereby lowering the insulating property. Since the epoxy equivalents of the epoxy resin can also react with the amide groups of the polyamideimide resin, this is preferably taken into account.

[0041]

As (c) antioxidant, one or more antioxidants from among hindered phenol-based antioxidants and organic sulfur compound-based antioxidants are used. Using a hindered phenol-based antioxidant can improve the electrical insulating characteristics without impairing the other properties such as drill working properties.

[0042]

Hindered phenol-based antioxidants include monophenol-based antioxidants such as butylated hydroxyanisole and 2,6-di-*t*-butyl-4-ethylphenol, bisphenol-based antioxidants such as 2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol), 4,4'-thiobis-(3-methyl-6-*t*-butylphenol) and 4,4'-butylidenebis(3-methyl-6-*t*-butylphenol), and high molecular phenols such as 1,1,3-tris(2-methyl-4-hydroxy-5-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene and tetrakis-[methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate]methane. Organic sulfur compound-

based antioxidants include dilauryl thiodipropionate, distearyl thiodipropionate and the like. Antioxidants are preferably one or more selected from the aforementioned group of antioxidants, and different types may be used in combination. The content of the (c) antioxidant is preferably 0.1-20 parts by weight to 100 parts by weight of the (b) thermosetting resin. More preferably, the content of the (c) antioxidant is 0.1-20 parts by weight to 100 parts by weight of the epoxy resin. If the content of the antioxidant is less than 0.1 part by weight no improvement in insulating property will be achieved, and if it exceeds 20 parts by weight the insulating property will tend to be reduced.

[0043]

The resin composition may also contain phosphorus-containing fillers for improvement of flame retardance in the present invention. As phosphorus-containing fillers there may be mentioned OP930 (product of Clariant Japan, phosphorus content: 23.5 wt%), HCA-HQ (product of Sanko Co., Ltd., phosphorus content: 9.6 wt%), and the melamine polyphosphates PMP-100 (phosphorus content: 13.8 wt%), PMP-200 (phosphorus content: 9.3 wt%) and PMP-300 (phosphorus content: 9.8 wt%) (all products of Nissan Chemical Industries, Ltd.). A larger amount of phosphorus-containing fillers will improve the flame retardance, but if it is too large the pliability of the base material will be reduced and the printed circuit board obtained therefrom will have reduced heat resistance. In this case, the amount of the phosphorus-containing fillers added to the resin composition is such for a phosphorus content of preferably 0.1-5 wt% and more

preferably 2-4 wt% of the total solid weight of the resin of the resin composition.

[0044]

The prepreg can be obtained by preparing a varnish by mixing, dissolving and dispersing a resin composition for prepreg in an organic solvent, and then impregnating it into a fiber material and drying in the present invention. The organic solvent is not particularly restricted so long as it is able to dissolve the resin composition, and as examples there may be mentioned dimethylacetamide, dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone,  $\gamma$ -butyrolactone, sulfolane and cyclohexanone.

[0045]

The resin composition for prepreg is preferably the resin composition containing 100 parts by weight of a siloxane-modified polyimide resin and 1-200 parts by weight of (b) thermosetting resin. This will increase the vaporization rate of the varnish solvent of the resin composition, making it possible to achieve a residual solvent content of 5 wt% or less even at a low temperature of below 150°C at which the thermosetting resin curing reaction is not promoted. As a result, the heat resistance adhesive seal have satisfactory adhesion between the fiber base material and copper foil. Since the highly heat resistant polyamideimide resin is modified by siloxane, the residual solvent can be decreased, the prepreg exhibits less swelling due to solvent vaporization during the step of lamination with the copper foil, and has excellent soldering heat resistance.

[0046]

The prepreg can be fabricated by impregnating the fiber base material with the resin composition varnish and drying it. The fiber base material is not particularly restricted so long as it is one used for fabrication of metal foil-clad laminates and multilayer printed circuit boards, and there may be mentioned fiber base materials such as woven fabrics and nonwoven fabrics. As materials for the fiber base material there may be mentioned inorganic fibers such as glass, alumina, asbestos, boron, silica-alumina glass, silica glass, tirano, silicon carbide, silicon nitride and zirconia, organic fibers such as aramid, polyetherether ketone, polyetherimide, polyethersulfone, carbon and cellulose, and blended systems thereof, among which woven fabrics of glass fibers are preferred. Among these, glass cloths with a thickness of 5-100  $\mu\text{m}$  are preferred as fiber base materials to be used in prepregs. By using a glass cloth with a thickness of 5-100  $\mu\text{m}$ , it is possible to obtain a printed circuit board that can be folded as desired, and which undergoes minimal dimensional change with the temperature and humidity of the manufacturing process.

[0047]

The manufacturing conditions for the prepreg are not particularly restricted, but preferred are conditions wherein at least 80 wt% of the solvent used in the varnish of resin composition evaporates. The fabrication process and drying conditions are also not particularly restricted, and for example, the temperature for drying may be 80-180°C, and the time may be adjusted in balance with the varnish gelling time. The impregnating amount of varnish is preferably such



for a varnish resin solid content of 30-80 wt% with respect to the total amount of resin solid of varnish and fiber base material.

[0048]

The manufacturing methods of insulating boards, laminates and metal foil-clad laminates are as follows. The prepreg of the present invention may be used alone or a plurality thereof laminated into a laminate, stacked with a metal foil on either or both sides as necessary, and subjected to hot pressure molding at a temperature in the range of 150-280°C or preferably 180-250°C, and a pressure in the range of 0.5-20 MPa or preferably 1-8 MPa, to fabricate an insulating board, laminate or metal foil-clad laminate. Using a metal foil to obtain metal foil-clad laminate, a printed circuit board can be obtained by forming a circuit to it.

[0049]

The metal foils used in the present invention include copper foils and aluminum foils, these metal foils having thicknesses of 5-200  $\mu\text{m}$  which are generally used to laminate can be applied. Copper foils is preferred. The metal foil may be a composite foil with a three-layer structure provided with an interlayer made of nickel, nickel-phosphorus, nickel-tin alloy, nickel-iron alloy, lead, lead-tin alloy or the like, having a 0.5-15  $\mu\text{m}$  copper layer and a 10-300  $\mu\text{m}$  copper layer on either side, or a composite foil with a two-layer structure comprising aluminum and copper foils.

[Examples]

[0050]

The present invention will now be explained in greater detail by examples, with the understanding that the invention is in no way limited to these examples.

(Synthesis Example 1)

5 In a 1-liter separable flask equipped with a cock-stoppered 25-ml water measuring receptacle connected to a reflux condenser, and a thermometer and stirrer, there were charged 12.4 g (0.05 mol) of DDS (diaminodiphenylsulfone) as a diamine with two or more aromatic rings, 51.6 g (0.06 mol) of the reactive silicone oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 430) as a siloxanediamine, 72.0 g (0.036 mol) of JEFFAMINE D2000 (trade name of San Techno Chemical Co., Ltd., amine equivalents: 1000), 10 11.34 g (0.054 mol) of WONDAMINE (trade name of New Japan Chemical Co., Ltd.) and 80.68 g (0.42 mol) of TMA (trimellitic anhydride), with 612 g of NMP (N-methyl-2-pyrrolidone) as an aprotic polar solvent, and the mixture was stirred at 80°C for 30 minutes. Next, 15 150 ml of toluene was loaded as an aromatic hydrocarbon for azeotropic distillation with water, and the temperature was raised for 2 hours of reflux at about 160°C. When approximately 7.2 ml of water had accumulated in the water measuring receptacle, cessation of water 20 distillation was confirmed, and the temperature was raised to about 190°C for removal of the toluene while removing the distillate accumulated in the water measuring receptacle. Next, the solution was returned to room temperature (25°C), and 60.1 g (0.24 mol) of MDI 25 (4,4'-diphenylmethanediisocyanate) was loaded as an aromatic diisocyanate for 2 hours of reaction at 190°C. Upon completion of the

reaction there was obtained an NMP solution containing a siloxane-modified polyamideimide resin.

[0051]

(Synthesis Example 2)

5 In a 1-liter separable flask equipped with a cock-stoppered 25-ml water measuring receptacle connected to a reflux condenser, and a thermometer and stirrer, there were charged 24.63 g (0.06 mol) of BAPP (2,2-bis[4-(4-aminophenoxy)phenyl]propane) as a diamine with two or more aromatic rings, 124.6 g (0.14 mol) of the reactive silicone  
10 oil KF-8010 (trade name of Shin-Etsu Chemical Co., Ltd., amine equivalents: 445) as a siloxanediamine and 80.68 g (0.42 mol) of TMA (trimellitic anhydride), with 539 g of NMP (N-methyl-2-pyrrolidone) as an aprotic polar solvent, and the mixture was stirred at 80°C for 30 minutes. Next, 150 ml of toluene was loaded as an aromatic  
15 hydrocarbon for azeotropic distillation with water, and the temperature was raised for 2 hours of reflux at about 160°C. When approximately 7.2 ml of water had accumulated in the water measuring receptacle, cessation of water distillation was confirmed, and the temperature was raised to about 190°C for removal of the toluene while removing the  
20 distillate accumulated in the water measuring receptacle. Next, the solution was returned to room temperature (25°C), and 60.07 g (0.24 mol) of MDI (4,4'-diphenylmethanediisocyanate) was loaded as an aromatic diisocyanate for 2 hours of reaction at 190°C. Upon completion of the reaction there was obtained an NMP solution  
25 containing a siloxane-modified polyamideimide resin.

[0052]

## (Example 1)

After mixing 218.75 g of an NMP solution of the siloxane-modified polyamideimide resin of Synthesis Example 1 (32 wt% solid resin content), 60.0 g of NC3000 (epoxy resin, trade name of Nippon Kayaku Co., Ltd.) as (b) thermosetting resin (dimethylacetamide solution with 50 wt% solid resin content), 0.3 g of 2-ethyl-4-methylimidazole and 0.5 g of 4,4'-butylidenebis(3-methyl-6-*t*-butylphenol) as (c) hindered phenol-based antioxidant, the mixture was stirred for about 1 hour until uniformity of the resin. Next, 20 g of OP930 (trade name of Clariant Japan) was added as a phosphorus-containing filler in the form of a slurry with 40 g of methyl ethyl ketone, and mixing was continued for one hour. The mixture was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

[0053]

## (Example 2)

After mixing 218.75 g of an NMP solution of the siloxane-modified polyamideimide resin of Synthesis Example 1 (32 wt% solid resin content), 60.0 g of DER331L (epoxy resin, trade name of The Dow Chemical Company) as (b) thermosetting resin (dimethylacetamide solution with 50 wt% solid resin content), 0.3 g of 2-ethyl-4-methylimidazole and 0.5 g of 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane as (c) hindered phenol-based antioxidant, the mixture was stirred for about 1 hour until uniformity of the resin. Next, 15 g of OP930 (trade name of Clariant Japan) was added as a phosphorus-containing filler in the form of a slurry with 30 g of methyl

ethyl ketone, and mixing was continued for one hour. The mixture was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

[0054]

5 (Example 3)

After mixing 218.75 g of an NMP solution of the siloxane-modified polyamideimide resin of Synthesis Example 1 (32 wt% solid resin content), 60.0 g of ZX-1548-2 (epoxy resin, trade name of Tohto Kasei Co., Ltd.) as (b) thermosetting resin (dimethylacetamide solution with  
10 50 wt% solid resin content), 0.3 g of 2-ethyl-4-methylimidazole and 0.5 g of dilauryl thiopropionate as (c) organic sulfur compound-based antioxidant, the mixture was stirred for about 1 hour until uniformity of the resin. Next, 20 g of OP930 (trade name of Clariant Japan) was added as a phosphorus-containing filler in the form of a slurry with 40  
15 g of methyl ethyl ketone, and mixing was continued for one hour. The mixture was then allowed to stand for 24 hours at room temperature (25°C) for defoaming to produce a resin composition varnish.

[0055]

(Example 4)

20 A resin composition varnish was produced in the same manner as Example 1, except that 200.0 g of an NMP solution of the siloxane-modified polyamideimide resin of Synthesis Example 2 (35 wt% solid resin content) was used instead of the siloxane-modified polyamideimide resin of Synthesis Example 1.

25 [0056]

(Example 5)

A resin composition varnish was produced in the same manner as Example 2, except that 200.0 g of an NMP solution of the siloxane-modified polyamideimide resin of Synthesis Example 2 (35 wt% solid resin content) was used instead of the siloxane-modified polyamideimide resin of Synthesis Example 1.

[0057]

(Comparative Example 1)

A resin composition varnish was produced in the same manner as Example 1, except for not adding the (c) hindered phenol-based antioxidant 4,4'-butylidenebis(3-methyl-6-t-butylphenol).

[0058]

(Comparative Example 2)

A resin composition varnish was produced in the same manner as Example 2, except for not adding the (c) hindered phenol-based antioxidant 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane.

[0059]

(Comparative Example 3)

A resin composition varnish was produced in the same manner as Example 3, except for not adding the (c) organic sulfur compound-based antioxidant dilauryl thiopropionate.

[0060]

(Comparative Example 4)

A resin composition varnish was produced in the same manner as Example 4, except for not adding the (c) hindered phenol-based antioxidant 4,4'-butylidenebis(3-methyl-6-t-butylphenol).

[0061]

(Comparative Example 5)

A resin composition varnish was produced in the same manner as Example 5, except for not adding the (c) hindered phenol-based antioxidant 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane.

5 [0062]

(Fabrication of prepreg and double-sided copper clad laminate)

The resin composition varnishes prepared in Examples 1-5 and Comparative Examples 1-5 were each impregnated into a 0.028 mm-thick glass cloth (trade name: 1037 by Asahi Shwebel Co., Ltd.), and  
10 then heated at 150°C for 15 minutes for drying to obtain a prepreg with a 70 wt% solid resin portion. A 12 µm-thick electrolytic copper foil (trade name: F2-WS-12 by Furukawa Electric Co., Ltd.) was stacked onto both sides of a prepreg with the adhesive sides facing the prepreg, and subjected to pressing conditions of 230°C, 90 min, 4.0 MPa to  
15 fabricate a double-sided copper clad laminate. Also, eight prepreps were stacked together, and a 12 µm-thick electrolytic copper foil (trade name: F2-WS-12 by Furukawa Electric Co., Ltd.) was stacked onto both sides thereof with the adhesive sides facing the prepreg, and then subjected to pressing conditions of 230°C, 90 min, 4.0 MPa to  
20 fabricate a double-sided copper clad laminate. The double-sided copper clad laminate fabricated with a single prepreg was subjected to the following evaluations (1) to (4). The double-sided copper clad laminate fabricated with eight prepreps was subjected to the following evaluations (5) and (6).

25 [0063]

(Evaluations)

(1) The copper foil peel strength of the double-sided copper clad laminate was measured.

(2) The time until abnormalities such as swelling or peeling appeared after immersion in soldering baths at 260°C and 300°C was measured.

5 (3) The copper foil was etched for removal and the laminate was folded to evaluate the pliability. ○: No fracture, △: Some fracture, ×: Fracture.

(4) The flame retardance was evaluated by a UL-94 VTM test. Specifically, first the copper was etched off from the double-sided  
10 copper clad laminate, and a 200 mm long, 50 mm wide piece was cut out and wrapped around a 12.7 mm-diameter mandrel, and after fixing it with tape at a position 125 mm from the end to form a cylinder, the mandrel was slipped out to obtain a sample. The sample was then situated vertically and the top end was closed and anchored with a  
15 spring, after which the bottom end was contacted with a 20 mm blue flame created with a methane gas burner for 3 seconds and the combustion distance was measured. Samples with a combustion distance of 100 mm or less were assigned a flame retardance of VTM-0.

20 (5) A circuit was formed on the double-sided copper clad laminate to prepare a daisy chain pattern test piece. Each test piece was subjected to 1000 cycles of a heat shock test with each cycle being -65°C/30 min, 125°C/30 min, and the change in resistance was measured. OK: No greater than 10% resistance change, NG: Greater than 10% resistance  
25 change.



(6) A circuit was formed on the double-sided copper clad laminate and used for a migration test. The through-holes were created with a 0.9 mm-diameter drill under conditions of 60,000 rpm, 1.800 mm/min feed rate. The spacing between hole walls was 350  $\mu\text{m}$ , and the insulation resistance of 400 holes (200 locations between through-hole/through-hole) was periodically measured for each sample. The test conditions were an environment of 85°C/90% RH and application of 100 V, and the measurement was carried out for a number of days until interruption of current between the through-holes occurred. Measurement of the insulation resistance was conducted at 100V/1 min, and interruption of current was defined as less than  $10^8 \Omega$ . The evaluation results are shown in Table 1.

[0064]

[Table 1]

Evaluation	Units	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Number of days to current interruption	Days	>60	>60	>60	>60	>60	30	7	10	35	11
Copper foil peel strength	kN/m	1.1	0.9	1.0	0.8	0.9	0.8	0.8	0.8	0.8	0.8
260°C soldering heat resistance	sec.	>300	>300	>300	>300	>300	>300	>300	>300	>300	>300
300°C soldering heat resistance	sec.	>300	>300	>300	>300	>300	>300	>300	>300	>300	>300
Heat shock test	-	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
Pliability	-	○	○	○	○	○	○	○	○	○	○
Flame retardance	-	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0	VTM-0

[0065]

The copper foil peel strengths of the double-sided copper clad laminates of Examples 1-5 were satisfactory high values of 0.8-1.1 kN/m. Also, the soldering heat resistance (260°C soldering, 300°C soldering) was 5 minutes or longer at both temperatures, and no abnormalities such as swelling or peeling were observed. The combustion distance of each 12.7 mm-diameter test piece in the UL94 VTM test was less than 100 mm, and the flame retardance was VTM-0 in all cases. In the heat shock test, the resistance change was within 10% at 1000 cycles, indicating satisfactory connection reliability. Also, the pliability was sufficient to allow folding as desired. Also, Examples 1-5 which included the (c) antioxidant exhibited no interruption of current for more than 60 days, and had higher insulation properties than Comparative Examples 1-5. The insulation resistance value was  $10^{11} \Omega$  or greater after 60 days with Examples 1-5.

[Document Name] Abstract

[Abstract]

[Problem] The present invention provide a printed circuit board which metal migration is hard to happen, with excellent dimensional stability and heat resistance and the ability to be bent and housed at high density in electronic device packages, as well as to provide a prepreg and metal foil-clad laminate which yield said printed circuit board.

[Means of Solution] A prepreg obtained by impregnating a resin composition into a fiber base material with a thickness of 5-100  $\mu\text{m}$ , wherein said resin composition is a resin composition comprising (a) a polyamideimide resin, (b) a thermosetting resin and (c) a hindered phenol-based antioxidant or an organic sulfur compound-based antioxidant.

[Selected Drawing] None